

Multicomponents system for modifying decomposing or bleaching of lignin or materials containing it or similar components and the way to use it

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Abstract

System for transforming, degrading or bleaching lignin, lignin-contg. materials or similar materials, comprises a poly-component system comprising: (a) opt. ≥ 1 oxidation catalyst; (b) ≥ 1 oxidising agent; (c) ≥ 1 mediator selected from hydroxylamines, hydroxylamine derivs., hydroxamic acids, hydroxamic acid derivs. and aliphatic, cycloaliphatic, heterocyclic and aromatic cpds. which contain ≥ 1 N-hydroxy, oxime, N-oxy or N,N-dioxy function; (d) opt. ≥ 1 co-mediator selected from aryl-substd. alcohols, carbonyl cpds., aliphatic ethers, phenol ethers and alkenes; and (e) a small amt. of a free amine of one of the mediators used.

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(54) Multi-Component System for Modifying, Degrading or Bleaching Lignin, Lignin-Containing Materials or Similar Substances and Processes for Its Use

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Notice: This application is as filed and may therefore contain an incomplete specification.



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MULTI-COMPONENT SYSTEM FOR MODIFYING, DEGRADING OR
BLEACHING LIGNIN, LIGNIN-CONTAINING MATERIALS OR
SIMILAR SUBSTANCES AND PROCESSES FOR ITS USE

ABSTRACT OF THE DISCLOSURE

The present invention relates to a multi-component system for modifying, degrading or bleaching lignin, lignin-containing materials or similar substances and to a process for its use. The multi-component system comprises if appropriate, at least one oxidation catalyst; and at least one suitable oxidizing agent; and at least one mediator chosen from the group consisting of hydroxylamines, hydroxylamine derivatives, hydroxamic acids, hydroxamic acid derivatives and aliphatic, cycloaliphatic, heterocyclic or aromatic compounds which contain at least one N-hydroxy, oxime, N-oxy or N,N.-dioxy function; and if appropriate, at least one comediator from the group consisting of aromatic alcohols, carbonyl compounds, aliphatic ethers, phenolic ethers and/or olefins (alkenes); and a small amount or at least one free amine of a mediator employed in each case.

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BACKGROUND OF THE INVENTION

The present invention relates to a multi-component system for modifying, degrading or bleaching lignin, lignin-containing materials or similar substances and to processes for its use.

The sulfate and the sulfite process are the processes currently primarily used for pulp production. With both processes, pulp is produced by cooking under pressure. The sulfate process operates with the addition of NaOH and Na₂S, while Ca(HSO₃)₂ + SO₂ is used in the sulfite process.

All the processes have the main objective of removing the lignin from the plant material, wood or annual plants used.

The lignin which, with the cellulose and the hemicellulose, makes up the main constituent of the plant material (stem or trunk) must be removed, since otherwise it is not possible to produce paper products which are non-yellowing and can be subjected to high mechanical stress.

Wood pulp production processes operate with stone grinders (mechanical wood pulp) or with refiners (TMP), which defibrillate the wood by grinding after appropriate pretreatment (chemical, thermal or chemical-thermal).

These wood pulps still comprise most of the lignin. They are used primarily for the production of newspapers, illustrated journals and the like.

The possibilities for using enzymes for degradation of lignin have been researched for some years. The action mechanism of such lignolytic systems was clarified only a few years ago, when it became possible to obtain adequate amounts of enzyme with the white rot fungus *Phanerochaete chrysosporium* under suitable growing conditions with additions of inductor. The previously unknown lignin peroxidases and manganese peroxidases were discovered by this research. Since *Phanerochaete chrysosporium* is a very effective degrader of lignin, attempts were made to isolate its enzymes and to use them in a suitable form for lignin degradation. However, this was not successful, since it was found that the enzymes lead above all to repolymerization of the lignin and not to degradation thereof.

Similar circumstances also apply to other lignolytic enzyme species, such as laccases, which degrade the lignin oxidatively with the aid of oxygen instead of hydrogen peroxide. It was found that similar processes occur in all cases. In fact, free radicals are formed which react with one another again and thus lead to polymerization.

There are thus currently only processes which operate with in vivo systems (fungus systems). The main key points of optimization experiments are so-called biopulping and biobleaching.

Biopulping is understood as meaning treatment of chopped wood chips with live fungus systems.

There are two types of biopulping application:

1. Pretreatment of chopped chips before refining or grinding in order to save energy during the production of wood pulps (for example TMP or mechanical wood pulp). Another advantage is the improvement which usually exists in the mechanical properties of the pulp, but a disadvantage is the poorer final brightness.

2. Pretreatment of chopped chips (softwood/hardwood) before cooking of the pulp (kraft process, sulfite process).

The aim is reduction in cooking chemicals, improvement in cooking capacity and "extended cooking".

Another advantage is an improved kappa reduction after cooking in comparison with cooking without pretreatment.

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Disadvantages of these processes are clearly the long treatment times (several weeks), and above all the unsolved risk of contamination during treatment if sterilization of the chopped chips, which is uneconomical, is to be dispensed with.

Biobleaching likewise operates with in vivo systems. The cooked pulp (softwood/hardwood) is seeded with fungus before bleaching and is treated for days to weeks. Only after this long treatment time is a significant reduction in kappa number and increase in brightness found, which renders the process uneconomical for implementation in the usual bleaching sequences.

Another application carried out usually with immobilized fungus systems is the treatment of waste waters from the manufacturer of pulp, in particular bleaching waste waters, for decolorization thereof and reduction of the AOX (reduction of chlorinated compounds in the waste water caused by chlorine or chlorine dioxide bleaching stages).

It is furthermore known to employ hemicellulases and also xylanases and mannanases as "bleaching boosters".

These enzymes are said to act chiefly against the xylan which is reprecipitated after the cooking process and partly masks the residual lignin, and degradation thereof increases the accessibility

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of the lignin to the bleaching chemicals (above all chlorine or chlorine dioxide) used in the subsequent bleaching sequences. The savings in bleaching chemicals demonstrated in the laboratory were confirmed to only a limited extent on a large scale, so that this type of enzyme can at best be classified as a bleaching additive.

Another possible use of lignolytic enzymes or fungi investigated recently has been recognized in "liquefaction of coal". Provisional studies show the main possibility of attacking and liquefying brown coal or hard coal with the aid of in vivo treatment, with, for example, white rot fungi, such as *Phanerochaete chrysosporium* (incubation time of several weeks). (Bio-engineering 4.92 Vol. 8).

The possible structure of hard coal shows a three-dimensional network of polycyclic aromatic ring systems with a "certain" similarity to lignin structures.

Chelating substances (siderophors, such as ammonium oxalate) and biosurfactants are assumed to be a cofactor, alongside the lignolytic enzymes.

The application PCT/EP87/00635 describes a system for removing lignin from material containing lignin-cellulose with simultaneous bleaching, which operates with lignolytic enzymes from

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white rot fungi with the addition of reducing and oxidizing agents and phenolic compounds as mediators.

In DE 4008893C2, "mimic substances" which simulate the active center (prosthetic group) of lignolytic enzymes are added in addition to the redox system. It was thus possible to achieve a considerable improvement in performance.

In the application PCT/EP92/01096, a redox cascade with the aid of phenolic or non-phenolic aromatics "coordinated" in oxidation potential is employed as an additional improvement.

The limitation for use on a large industrial scale is the applicability at low pulp densities (up to not more than 4%) for all three processes, and for the last two applications the risk of "leaching out" of metals when using chelating compounds, which can lead above all to destruction of the peroxide in the subsequent peroxide bleaching stages.

Processes in which the activity of peroxidase is promoted by means of so-called enhancer substances are known from WO 94/12619, WO 94/12620, and WO 94/12621.

The enhancer substances are characterized with the aid of their half-life in WO 94/12619.

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According to NO 94/12620, enhancer substances are characterized by the formula $A-N-N-B$, in which A and B are each defined cyclic group.

According to NO 94/12620, enhancer substances are organic chemicals which contain at least two aromatic rings, at least one of which is substituted by in each case defined groups.

All three applications relate to "dye transfer inhibition" and the use of the particular enhancer substances, together with peroxidases, as a detergent additive or detergent composition in the detergent sector. Although a possible use for treatment of lignin is referred to in the description of the application, our own experiments with the substances disclosed completely in the application have shown that they showed no activity as mediators for increasing the bleaching action of the peroxidases during treatment of lignin-containing materials.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a system for modifying, degrading or bleaching lignin, lignin-containing materials or similar substances which is more effective than known systems.

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The above object is achieved according to the present invention by a multi-component system, which comprises:

- a. if appropriate at least one oxidation catalyst, and
- b. at least one suitable oxidizing agent, and
- c. at least one mediator selected from the group consisting of hydroxylamines, hydroxylamine derivatives, hydroxamic acids, hydroxamic acid derivatives and aliphatic, cycloaliphatic, heterocyclic or aromatic compounds which contain at least one N-hydroxy, oxime, N-oxy or N, N'-dioxy function, and
- d. if appropriate, at least one comediator selected from the group consisting of aryl-substituted alcohols, carbonyl compounds, aliphatic ethers, phenolic ethers and/or olefins (alkenes), and
- e. a small amount of at least one free amine of a mediator employed in each case.

The multi-component system according to the invention preferably comprises at least one oxidation catalyst.

The multi-component system according to the invention preferably comprises at least one comediator.

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Enzymes are preferably employed as oxidation catalysts in the multi-component system according to the invention. In the context of the invention, the term enzyme also includes enzymatically active proteins or peptides or prosthetic groups of enzymes.

Enzymes which can be employed in the multi-component system according to the invention are oxidoreductases of classes 1.1.1 to 1.97 according to *International Enzyme Nomenclature, Committee of the International Union of Biochemistry and Molecular Biology (Enzyme Nomenclature, Academic Press, Inc., 1992, pages 24-154)*.

The enzymes of the classes mentioned below are preferably employed:

Enzymes of class 1.1, which include all dehydrogenases which act on primary alcohols and secondary alcohols and semiacetals and have NAD⁺ or NADP (subclass 1.1.1), cytochromes (1.1.2), oxygen (O₂) (1.1.3), disulfides (1.1.4), quinones (1.1.5) as acceptors or have other acceptors (1.1.99).

Enzymes of this class which are particularly preferred are those of class 1.1.5 with quinones as acceptors and enzymes of class 1.1.3 with oxygen as the acceptor.

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Cellobiose: quinone-1-oxidoreductase (1.1.5.1) is particularly preferred in this class.

Enzymes of class 1.2 are furthermore preferred. This enzyme class (1.1.5.1) includes those enzymes which oxidize aldehydes to give the corresponding acids or oxo groups. The acceptors can be NAD⁺, NADP⁺ (1.2.1), cytochromes (1.2.2), oxygen (1.2.3), sulfides (1.2.4), iron/sulfur proteins (1.2.5), or other acceptors (1.2.99).

The enzymes of group (1.2.3) with oxygen as the acceptor are particularly preferred here.

Enzymes of class 1.3 are furthermore preferred.

This class comprises enzymes which act on CH-CH groups of the donor.

The corresponding acceptors are NAD⁺, NADP⁺ (1.3.1), cytochromes (1.3.2), oxygen (1.3.3), quinones or related compounds (1.3.5), iron/sulfur proteins (1.3.7), or other acceptors (1.3.99).

Here also, the enzymes of class (1.3.3) with oxygen as the acceptor and (1.3.5) with quinones and the like as the acceptor are particularly preferred.

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Enzymes of class 1.4 which act on $\text{C}=\text{NH}_2$ groups of the donor are furthermore preferred.

The corresponding acceptors are NAD^+ , NADP^+ (1.4.1), cytochromes (1.4.2), oxygen (1.4.3), disulfides (1.4.4), iron/sulfur proteins (1.4.7), or other acceptors (1.4.99).

Enzymes of class 1.4.3 with oxygen as the acceptor are also particularly preferred here.

Enzymes of class 1.5 which act on $\text{CH}-\text{NH}$ groups or the donor are furthermore preferred. The corresponding acceptors are NAD^+ , NADP^+ (1.5.1), oxygen (1.5.3), disulfides (1.5.4), quinones (1.5.5), or other acceptors (1.5.99).

Enzymes with oxygen (O_2) (1.5.3) and with quinones (1.5.5) as acceptors are also particularly preferred here.

Enzymes of class 1.6 which act on NADH or NADPH are furthermore preferred.

The acceptors here are NADP^+ (1.6.1), hemoproteins (1.6.2), disulfides (1.6.4), quinones (1.6.5), NO_2 groups (1.6.6) and a flavin (1.6.8), or some other acceptors (1.6.99).

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Enzymes of class 1.6.5 with quinones as acceptors are particularly preferred here.

Enzymes which are furthermore preferred are those of class 1.7 which act on other NO_2 compounds as donors and have cytochromes (1.7.2), oxygen (O_2), (1.7.3), iron/sulfur proteins (1.7.7), or others (1.7.99) as acceptors.

Class 1.7.3 with oxygen as the acceptor is particularly preferred here.

Enzymes which are furthermore preferred are those of class 1.8 which act on sulfur groups as donors and have NAD-, NADP- (1.8.1), cytochromes (1.8.2), oxygen (O_2) (1.8.3), disulfides (1.8.4), quinones (1.8.5), iron/sulfur proteins (1.8.7), or others (1.8.99) as acceptors.

Class 1.8.3 with oxygen (O_2) and (1.8.5) with quinones as acceptors is particularly preferred.

Enzymes which are furthermore preferred are those of class 1.9 which have heme groups as donors and have oxygen (O_2) (1.9.3), NO_2 compounds (1.9.6) and others (1.9.99) as acceptors.

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Group 1.9.3 with oxygen (O_2) as the acceptor (cytochrome oxidases) is particularly preferred here.

Enzymes of class 1.12 which act on hydrogen as the donor are furthermore preferred.

The acceptors are NAD^+ or $NADP^+$ (1.12.1) or others (1.12.99).

Enzymes of class 1.13 and 1.14 (oxygenases) are furthermore preferred.

Enzymes which are furthermore preferred are those of class 1.15 which act on superoxide radicals as acceptors.

Superoxide dismutase (1.15.1.1) is particularly preferred here.

Enzymes of class 1.16 are furthermore preferred.

NAD^+ or $NADP^+$ (1.16.1) or oxygen (O_2) (1.16.3) act as acceptors.

Enzymes of class 1.16.3.1 (ferroxidase, for example ceruloplasmin) are particularly preferred here.

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Enzymes which are furthermore preferred are those which belong to group 1.17 (action on CH_2 groups, which are oxidized to - CHOH-), 1.18 (action on reduced ferredoxin as the donor), 1.19 (action on reduced flavodoxin as the donor) and 1.97 (other oxidoreductases).

The enzymes of group 1.11 which act on a peroxide as the acceptor are furthermore particularly preferred. This sole subclass (1.11.1) contains the peroxidases.

Enzymes which are particularly preferred here are the cytochrome C peroxidases (1.11.1.5), catalase (1.11.1.6), peroxidase (1.11.1.6), iodide peroxidase (1.11.1.8), glutathione peroxidase (1.11.1.9), chloride peroxidase (1.11.1.10), L-ascorbate peroxidase (1.11.1.11), phospholipid hydroperoxide glutathione peroxidase (1.11.1.12), manganese peroxidase (1.11.1.13) and diarylpropane peroxidase (ligninase, lignin peroxidase (1.11.1.14)).

The enzymes of class 1.10 which act on biphenols and related compounds are especially preferred. They catalyze the oxidation of biphenols and ascorbates. NAD^+ , NADP^+ (1.10.1), cytochromes (1.10.2), oxygen (1.10.3) or others (1.10.99) function as acceptors.

Enzymes of class 1.10.3 with oxygen (O_2) as the acceptor are in turn particularly preferred among these.

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Particularly preferred enzymes of this class are the enzymes catechol oxidase (tyrosinase) (1.10.3.1), L-ascorbate oxidase (1.10.3.3), o-aminophenol oxidase (1.10.3.4) and laccase (benzenediol:oxygen oxidoreductase) (1.10.3.2). the laccases (benzenediol:oxygen oxidoreductase) (1.10.3.2) being particularly preferred.

These enzymes are commercially obtainable or can be obtained by standard processes. Possible organisms for production of the enzymes are, for example, plants, animal cells, bacteria and fungi. In principle, both naturally occurring organisms and organisms modified by genetic engineering can be producers of enzymes. Parts of one-cell or multicell organisms, above all cell cultures, are also conceivable as producers of enzymes.

White rot fungi, such as *Pleurotus*, *Phlebia* and *Trametes*, for example, are used for the particularly preferred enzymes, such as those from group 1.11.1, but above all 1.10.3, and in particular for the production of laccases.

The multi-component system according to the invention comprises at least one oxidizing agent. Oxidizing agents which can be employed are, for example, air, oxygen, ozone, H_2O_2 , organic peroxides, peracids, such as peracetic acid, performic acid, persulfuric acid, pernitric acid, metachloroperoxybenzoic acid and perchloric acid,

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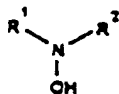
perborates, peracetates, persulfates, peroxides or oxygen species and free radicals thereof, such as OH, OOH, superoxide (O_2^-) singlet oxygen, ozonide, the dicxygenyl cation (O_2^+), dioxirane, dioxetanes or Fremy radicals.

Those oxidizing agents which either can be generated by the corresponding oxidoreductases, for example dioxiranes from laccases plus carbonyls, or which can regenerate the mediator chemically (for example Caro's acid + benzotriazole gives hydroxybenzotriazole) or can react with the mediator directly are preferably employed.

The multi-component system according to the invention comprises, as the mediator (component c), preferably at least one compound which contains at least one N-hydroxy, oxime, N-oxy or N-dioxy function and/or one of the compounds of the formula I, II, III, IV, or V mentioned below, the compounds of the formulae II, III, IV and V being preferred, the compounds of the formulae III, IV and V being particularly preferred and compounds of the formulae IV and V being especially preferred.

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Hydroxylamines: (open-chain or cyclic, aliphatic or aromatic, heterocyclic) of the general formula I



I

in which, in the general formula I, the substituents R^1 and R^2 , which can be identical or different, independently of one another are one of the following groups: hydrogen, C_1-C_{12} -alkyl, carbonyl- C_1-C_6 -alkyl, phenyl or aryl, the C_1-C_{12} -alkyl, carbonyl- C_1-C_6 -alkyl, phenyl or aryl, of which can be unsubstituted or furthermore mono- or polysubstituted by the radical R^3 , and in which the radical R^3 can be one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, sulfono, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and salts and esters thereof, in which the amino, carbamoyl and sulfamoyl groups of the radical R^3 furthermore can be unsubstituted or mono- or disubstituted by hydroxyl, C_1-C_6 -alkyl or C_1-C_6 -alkoxy, and in which the radicals R^1 and R^2 together can form a group $-B-$, and $-B-$ is one of the following groups: $(-CHR^4-)_n$, or $(-CR^4=CH-)_m$, and in which R^4 is a substituent which is defined as R^3 , and n is an integer from 1 to 6 and m is an integer from 1 to 3.

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Examples:

Hydroxylamines

N,N-dipropylhydroxylamine

N,N-diisopropylhydroxylamine

N-hydroxypyrrolidine

N-hydroxypiperidine

N-hydroxyhexahydroazepine

N,N-dibenzylhydroxylamine

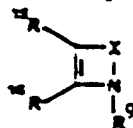
phenylhydroxylamine

3-hydroxylamino-3-phenylpropionic acid

2-hydroxylamino-3-phenylpropionic acid

N-sulfomethylhydroxylamine

Compounds of the general formula II are:



in which X is one of the following groups: $(-N=N-)$,

$(-N=CR^{10}-)$, $(-CR^{10}=N-)$, $(-CR^{11}=CR^{12}-)$,



in which the radicals R^1 to R^9 , R^{10} and R^{11} can be identical or

different and independently of one another can be one of the following

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groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_4 -alkyloxy, carbonyl- C_1-C_4 -alkyl, phenyl, sulfono, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphenoxy and salts and esters thereof, and in which the amino, carbamoyl and sulfamoyl groups of the radicals R^1 to R^{12} , R^{13} and R^{14} furthermore can be unsubstituted or mono- or disubstituted by hydroxyl, C_1-C_4 -alkyl or C_1-C_4 -alkoxy, and in which the radicals R^{13} and R^{14} can form a common group -G- and -G- here is one of the following groups: $(-CR^1=CR^2-CR^3=CR^4-)$ or $(-CR^1=CR^2-CR^3-CR^4-)$.

The radicals R^1 to R^4 can be identical or different and independently of one another are one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_4 -alkyloxy, carbonyl- C_1-C_4 -alkyl, phenyl, sulfono, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphenoxy and salts and esters thereof, and in which the amino, carbamoyl and sulfamoyl groups of the radicals R^1 to R^4 furthermore can be unsubstituted or mono- or disubstituted by hydroxyl, C_1-C_4 -alkyl or C_1-C_4 -alkoxy, and in which the C_1-C_{12} -alkyl, C_1-C_4 -alkyloxy, carbonyl- C_1-C_4 -alkyl, phenyl and aryl groups of the radicals R^1 to R^4 can be unsubstituted or furthermore mono- or polysubstituted by the radical R^{15} , and in which the radical R^{15} can be one of the following groups: hydrogen, halogen, hydroxyl,

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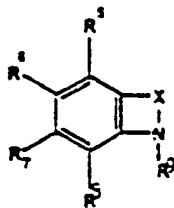
formyl, carboxyl and salts and esters thereof, amino, nitro, C₁-C₁₂-alkyl, C₁-C₄-alkyloxy, carbonyl-C₁-C₄-alkyl, phenyl, aryl, and esters and salts thereof, and in which the carbamoyl, sulfamoyl and amino groups of the radical R¹ can be unsubstituted or furthermore mono- or disubstituted by the radical R², and in which the radical R² can be one of the following groups: hydrogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C₁-C₁₂-alkyl, C₁-C₄-alkyloxy, carbonyl-C₁-C₄-alkyl, phenyl and aryl.

Examples:

- 1-hydroxy-1,2,3-triazole-4,5-dicarboxylic acid
- 1-phenyl-1H-1,2,3-triazole 3-oxide
- 5-chloro-1-phenyl-1H-1,2,3-triazole 3-oxide
- 5-methyl-1-phenyl-1H-1,2,3-triazole 3-oxide
- 4-(2,2-dimethylpropanoyl)-1-hydroxy-1H-1,2,3-triazole
- 4-hydroxy-2-phenyl-2H-1,2,3-triazole 1-oxide
- 2,4,5-triphenyl-2H-1,2,3-triazole 1-oxide
- 1-benzyl-1H-1,2,3-triazole 3-oxide
- 1-benzyl-4-chloro-1H-1,2,3-triazole 3-oxide
- 1-benzyl-4-bromo-1H-1,2,3-triazole 3-oxide
- 1-benzyl-4-methoxy-1H-1,2,3-triazole 3-oxide

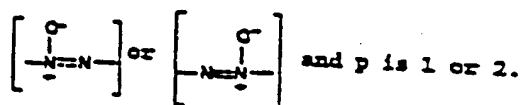
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Compounds of the general structure III are:



III

in which X is one of the following groups: (-N=N-),
(-N=CR¹⁰-), (-CR¹⁰=N-), (-CR¹¹=CR¹²-),



The radicals R¹ to R¹² can be identical or different and independently of one another are one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C₁-C₁₂-alkyl, C₁-C₄-alkyloxy, carbonyl-C₁-C₄-alkyl, phenyl, aryl, sulfono, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and salts and esters thereof, and in which the amino, carbamoyl and sulfamoyl groups of the radicals R¹ to R¹² furthermore can be unsubstituted or mono- or disubstituted by hydroxyl, C₁-C₄-alkyl or C₁-C₄-alkoxy, and in which the C₁-C₁₂-alkyl, C₁-C₄-alkyloxy, carbonyl-C₁-C₄-alkyl, phenyl, aryl, and aryl-C₁-C₄-alkyl groups of the radicals R¹ to R¹² can be unsubstituted or furthermore mono- or polysubstituted by the radical R¹¹, and in

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which the radical R^{13} can be one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, aryl, sulfono, sulfeno, sulfinio and esters and salts thereof, and in which the carbamoyl, sulfamoyl and amino groups of the radical R^{13} can be unsubstituted or furthermore mono-or disubstituted by the radical R^{14} , and in which the radical R^{14} can be one of the following groups: hydrogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, or aryl.

Examples:

1-Hydroxy-benzimidazoles

1-hydroxybenzimidazole-2-carboxylic acid

1-hydroxybenzimidazole

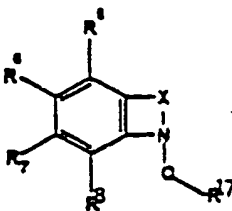
2-methyl-1-hydroxybenzimidazole

2-phenyl-1-hydroxybenzimidazole

1-Hydroxyindoles

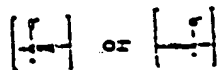
2-phenyl-1-hydroxyindole

Substances of the general formula IV are:



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in which X is one of the following groups: $(-N=N-)$,
 $(-N=CR^{10}-)_m$, $(-CR^{10}=N-)_m$, $(-CR^{11}=CR^{12}-)_m$

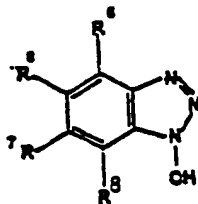


and m is 1 or 2.

The above statements apply to the radicals R^1 to R^4 and
 R^{10} to R^{12} .

R^{17} can be: hydrogen, C_1 - C_{10} -alkyl or
 C_1 - C_{10} -alkyl-carbonyl, the C_1 - C_{10} -alkyl and C_1 - C_m -alkylcarbonyl of which
 can be unsubstituted or mono- or polysubstituted by a radical R^{18} ,
 which is defined as R^1 .

Preferred substances of the formula IV are, in
 particular, derivatives of 1-hydroxybenzotriazole and of the
 tautomeric benzotriazole 1-oxide and esters and salts thereof
 (compounds of the formula V)



V

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The radicals R^1 to R^4 can be identical or different and independently of one another are one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, sulfono, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and salts and esters thereof, and in which the amino, carbamoyl and sulfamoyl groups of the radicals R^1 to R^4 , furthermore can be unsubstituted or mono- or disubstituted by hydroxyl, C_1-C_6 -alkyl or C_1-C_6 -alkoxy, and in which the C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl and aryl groups of the radicals R^1 and R^2 can be unsubstituted or furthermore mono- or polysubstituted by the radical R^{11} , and in which the radical R^{11} can be one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, aryl, sulfono, sulfeno, sulfino, and esters and salts thereof, and in which the carbamoyl, sulfamoyl, and amino groups of the radical R^{11} can be unsubstituted or furthermore mono- or disubstituted by the radical R^{12} , and in which the radical R^{12} can be one of the following groups: hydrogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl and aryl.

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Examples:

1H-Hydroxybenzotriazoles

1-hydroxybenzotriazole

1-hydroxybenzotriazole, sodium salt

1-hydroxybenzotriazole, potassium salt

1-hydroxybenzotriazole, lithium salt

1-hydroxybenzotriazole, ammonium salt

1-hydroxybenzotriazole, calcium salt

1-hydroxybenzotriazole, magnesium salt

1-hydroxybenzotriazole-6-sulfonic acid

1-hydroxybenzotriazole-6-sulfonic acid, monosodium salt

1-hydroxybenzotriazole-6-carboxylic acid

1-hydroxybenzotriazole-6-N-phenylcarboxamide

5-ethoxy-6-nitro-1-hydroxybenzotriazole

4-ethyl-7-methyl-6-nitro-1-hydroxybenzotriazole

2,3-bis-(4-ethoxyphenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole

2,3-bis-(2-bromo-4-methylphenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole

2,3-bis-(4-bromophenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole

2,3-bis-(4-carboxyphenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole

4,6-bis-(trifluoromethyl)-1-hydroxybenzotriazole

5-bromo-1-hydroxybenzotriazole

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6-bromo-1-hydroxybenzotriazole
4-bromo-7-methyl-1-hydroxybenzotriazole
5-bromo-7-methyl-6-nitro-1-hydroxybenzotriazole
4-bromo-6-nitro-1-hydroxybenzotriazole
6-bromo-4-nitro-1-hydroxybenzotriazole
4-chloro-1-hydroxybenzotriazole
5-chloro-1-hydroxybenzotriazole
6-chloro-1-hydroxybenzotriazole
6-chloro-5-isopropyl-1-hydroxybenzotriazole
5-chloro-6-methyl-1-hydroxybenzotriazole
6-chloro-5-methyl-1-hydroxybenzotriazole
4-chloro-7-methyl-6-nitro-1-hydroxybenzotriazole
4-chloro-5-methyl-1-hydroxybenzotriazole
5-chloro-4-methyl-1-hydroxybenzotriazole
4-chloro-6-nitro-1-hydroxybenzotriazole
6-chloro-4-nitro-1-hydroxybenzotriazole
7-chloro-1-hydroxybenzotriazole
6-diacetylamino-1-hydroxybenzotriazole
2,3-dibenzyl-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole
4,6-dibromo-1-hydroxybenzotriazole
4,6-dichloro-1-hydroxybenzotriazole
5,6-dichloro-1-hydroxybenzotriazole
4,5-dichloro-1-hydroxybenzotriazole
4,7-dichloro-1-hydroxybenzotriazole
5,7-dichloro-6-nitro-1-hydroxybenzotriazole

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5,6-dimethoxy-1-hydroxybenzotriazole
2,3-di-(2)naphthyl-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole
4,6-dinitro-1-hydroxybenzotriazole
4,6-dinitro-2,3-diphenyl-2,3-dihydro-1-hydroxybenzotriazole
4,6-dinitro-2,3-di-p-tolyl-2,3-dihydro-1-hydroxybenzotriazole
5-hydrazino-7-methyl-4-nitro-1-hydroxybenzotriazole
5,6-dimethyl-1-hydroxybenzotriazole
4-methyl-1-hydroxybenzotriazole
5-methyl-1-hydroxybenzotriazole
6-methyl-1-hydroxybenzotriazole
5-(1-methylethyl)-1-hydroxybenzotriazole
4-methyl-6-nitro-1-hydroxybenzotriazole
6-methyl-4-nitro-1-hydroxybenzotriazole
5-methoxy-1-hydroxybenzotriazole
6-methoxy-1-hydroxybenzotriazole
7-methyl-6-nitro-1-hydroxybenzotriazole
4-nitro-1-hydroxybenzotriazole
6-nitro-1-hydroxybenzotriazole
6-nitro-4-phenyl-1-hydroxybenzotriazole
5-phenylmethyl-1-hydroxybenzotriazole
4-trifluoromethyl-1-hydroxybenzotriazole
5-trifluoromethyl-1-hydroxybenzotriazole
6-trifluoromethyl-1-hydroxybenzotriazole
4,5,6,7-tetrachloro-1-hydroxybenzotriazole
4,5,6,7-tetrafluoro-1-hydroxybenzotriazole

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6-tetrafluoroethyl-1-hydroxybenzotriazole
4,5,6-trichloro-1-hydroxybenzotriazole
4,6,7-trichloro-1-hydroxybenzotriazole
6-sulfamido-1-hydroxybenzotriazole
6-N,N-diethyl-sulfamido-1-hydroxybenzotriazole
6-N-methylsulfamido-1-hydroxybenzotriazole
6-(1H-1,2,4-triazol-1-ylmethyl)-1-hydroxybenzotriazole
6-(5,6,7,8-tetrahydroimidazo-[1,5-a]-pyridin-5-yl)-1-hydroxybenzotriazole
6-(phenyl-1H-1,2,4-triazol-1-ylmethyl)-1-hydroxybenzotriazole
6-[(5-methyl-1H-imidazo-1-yl)-phenylmethyl]-1-hydroxybenzotriazole
6-[(4-methyl-1H-imidazo-1-yl)-phenylmethyl]-1-hydroxybenzotriazole
6-[(2-methyl-1H-imidazo-1-yl)-phenylmethyl]-1-hydroxybenzotriazole
6-(1H-imidazol-1-yl-phenylmethyl)-1-hydroxybenzotriazole
5-(1H-imidazol-1-yl-phenylmethyl)-1-hydroxybenzotriazole
6-[1-(1H-imidazol-1-yl)-ethyl]-1-hydroxybenzotriazole
monohydrochloride

3H-Benzotriazole 1-oxides
3H-benzotriazole 1-oxide
6-acetyl-3H-benzotriazole 1-oxide
5-ethoxy-6-nitro-3H-benzotriazole 1-oxide
4-ethyl-7-methyl-6-nitro-3H-benzotriazole 1-oxide
6-amino-3,5-dimethyl-3H-benzotriazole 1-oxide
6-amino-3-methyl-3H-benzotriazole 1-oxide

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5-bromo-3H-benzotriazole 1-oxide
6-bromo-3H-benzotriazole 1-oxide
4-bromo-7-methyl-3H-benzotriazole 1-oxide
5-bromo-4-chloro-6-nitro-3H-benzotriazole 1-oxide
4-bromo-6-nitro-3H-benzotriazole 1-oxide
6-bromo-4-nitro-3H-benzotriazole 1-oxide
5-chloro-3H-benzotriazole 1-oxide
6-chloro-3H-benzotriazole 1-oxide
4-chloro-6-nitro-3H-benzotriazole 1-oxide
4,6-dibromo-3H-benzotriazole 1-oxide
4,6-dibromo-3-methyl-3H-benzotriazole 1-oxide
4,6-dichloro-3H-benzotriazole 1-oxide
4,7-dichloro-3H-benzotriazole 1-oxide
5,6-dichloro-3H-benzotriazole 1-oxide
4,6-dichloro-3-methyl-3H-benzotriazole 1-oxide
5,7-dichloro-6-nitro-3H-benzotriazole 1-oxide
3,6-dimethyl-6-nitro-3H-benzotriazole 1-oxide
3,5-dimethyl-6-nitro-3H-benzotriazole 1-oxide
3-methyl-3H-benzotriazole 1-oxide
5-methyl-3H-benzotriazole 1-oxide
6-methyl-3H-benzotriazole 1-oxide
6-methyl-4-nitro-3H-benzotriazole 1-oxide
7-methyl-6-nitro-3H-benzotriazole 1-oxide
5-chloro-6-nitro-3H-benzotriazole 1-oxide

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2H-Benzotriazole 1-oxides

2-(4-acetoxyphenyl)-2H-benzotriazole 1-oxide
6-acetylamino-2-phenyl-2H-benzotriazole 1-oxide
2-(4-ethylphenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
2-(3-aminophenyl)-2H-benzotriazole 1-oxide
2-(4-aminophenyl)-2H-benzotriazole 1-oxide
6-amino-2-phenyl-2H-benzotriazole 1-oxide
5-bromo-4-chloro-6-nitro-2-phenyl-2H-benzotriazole 1-oxide
2-(4-bromophenyl)-2H-benzotriazole 1-oxide
5-bromo-2-phenyl-2H-benzotriazole 1-oxide
6-bromo-2-phenyl-2H-benzotriazole 1-oxide
2-(4-bromophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
2-(4-bromophenyl)-6-nitro-2H-benzotriazole 1-oxide
5-chloro-2-(2-chlorophenyl)-2H-benzotriazole 1-oxide
5-chloro-2-(3-chlorophenyl)-2H-benzotriazole 1-oxide
5-chloro-2-(2-chlorophenyl)-2H-benzotriazole 1-oxide
5-chloro-2-(3-chlorophenyl)-2H-benzotriazole 1-oxide
5-chloro-2-(2,4-dibromophenyl)-2H-benzotriazole 1-oxide
5-chloro-2-(2,5-dimethylphenyl)-2H-benzotriazole 1-oxide
5-chloro-2-(4-nitrophenyl)-2H-benzotriazole 1-oxide
5-chloro-6-nitro-2-phenyl-2H-benzotriazole 1-oxide
2-[4-(4-chloro-3-nitrophenylazo)-3-nitrophenyl]-4,6-dinitro-2H-benzotriazole 1-oxide
2-(3-chloro-4-nitrophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide

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2-(4-chloro-3-nitrophenyl)-4,6-dinitro-2H-benzotriazole
1-oxide
4-chloro-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
5-chloro-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
6-chloro-4-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
2-(2-chlorophenyl)-2H-benzotriazole 1-oxide
2-(3-chlorophenyl)-2H-benzotriazole 1-oxide
2-(4-chlorophenyl)-2H-benzotriazole 1-oxide
5-chloro-2-phenyl-2H-benzotriazole 1-oxide
2-[4-(4-chlorophenylazo)-3-nitrophenyl]-4,6-dinitro-2H-benzotriazole
1-oxide
2-(2-chlorophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
2-(3-chlorophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
2-(4-chlorophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
2-[4-(N'-(3-chlorophenyl)-hydrazino)-3-nitrophenyl]-4,6-dinitro-2H-
benzotriazole 1-oxide
2-[4-(N'-(4-chlorophenyl)-hydrazino)-3-nitrophenyl]-4,6-dinitro-2H-
benzotriazole 1-oxide
2-(2-chlorophenyl)-6-methyl-2H-benzotriazole 1-oxide
2-(3-chlorophenyl)-6-methyl-2H-benzotriazole 1-oxide
2-(4-chlorophenyl)-6-methyl-2H-benzotriazole 1-oxide
2-(3-chlorophenyl)-6-nitro-2H-benzotriazole 1-oxide
2-(4-chlorophenyl)-6-nitro-2H-benzotriazole 1-oxide
2-(4-chlorophenyl)-6-picrylazo-2H-benzotriazole 1-oxide
5-chloro-2-(2,4,5-trimethylphenyl)-2H-benzotriazole 1-oxide

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4,5-dibromo-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
4,5-dichloro-6-nitro-2-phenyl-2H-benzotriazole 1-oxide
4,5-dichloro-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
4,7-dichloro-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
4,7-dimethyl-6-nitro-2-phenyl-2H-benzotriazole 1-oxide
2-(2,4-dimethylphenyl)-4,6-dinitro-benzotriazole 1-oxide
2-(2,5-dimethylphenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
2-(2,4-dimethylphenyl)-6-nitro-2H-benzotriazole 1-oxide
2-(2,5-dimethylphenyl)-6-nitro-2H-benzotriazole 1-oxide
4,6-dinitro-2-[3-nitro-4-(N'-phenylhydrazino)-phenyl]-2H-benzotriazole
1-oxide
4,6-dinitro-2-[4-nitro-4-(N'-phenylhydrazino)-phenyl]-2H-benzotriazole
1-oxide
4,6-dinitro-2-phenyl-2H-benzotriazole 1-oxide
2-(2,4-dinitrophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
2-(2,4-dinitrophenyl)-6-nitro-2H-benzotriazole 1-oxide
4,6-dinitro-2-o-tolyl-2H-benzotriazole 1-oxide
4,6-dinitro-2-p-tolyl-2H-benzotriazole 1-oxide
4,6-dinitro-2-(2,4,5-trimethylphenyl)-2H-benzotriazole 1-oxide
2-(4-methoxyphenyl)-2H-benzotriazole 1-oxide
2-(4-methoxyphenyl)-6-methyl-2H-benzotriazole 1-oxide
5-methyl-6-nitro-2-m-tolyl-2H-benzotriazole 1-oxide
5-methyl-6-nitro-2-o-tolyl-2H-benzotriazole 1-oxide
5-methyl-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
6-methyl-4-nitro-2-p-tolyl-2H-benzotriazole 1-oxide

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6-methyl-2-phenyl-2H-benzotriazole 1-oxide
4-methyl-2-m-tolyl-2H-benzotriazole 1-oxide
4-methyl-2-o-tolyl-2H-benzotriazole 1-oxide
4-methyl-2-p-tolyl-2H-benzotriazole 1-oxide
6-methyl-2-m-tolyl-2H-benzotriazole 1-oxide
6-methyl-2-o-tolyl-2H-benzotriazole 1-oxide
6-methyl-2-p-tolyl-2H-benzotriazole 1-oxide
2-naphth-1-yl-4,6-dinitro-2H-benzotriazole 1-oxide
2-naphth-2-yl-4,6-dinitro-2H-benzotriazole 1-oxide
2-naphth-1-yl-6-nitro-2H-benzotriazole 1-oxide
2-naphth-2-yl-6-nitro-2H-benzotriazole 1-oxide
2-(3-nitrophenyl)-2H-benzotriazole 1-oxide
6-nitro-2-phenyl-2H-benzotriazole 1-oxide
4-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
6-nitro-2-o-tolyl-2H-benzotriazole 1-oxide
6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
6-nitro-2-(2,4,5-trimethylphenyl)-2H-benzotriazole 1-oxide
2-phenyl-2H-benzotriazole 1-oxide
2-o-tolyl-2H-benzotriazole 1-oxide
2-p-tolyl-2H-benzotriazole 1-oxide

Compounds which are furthermore preferred are heterocyclic compounds which contain at least one N-hydroxyl, oxime, N-oxy or N,N-dioxy function and a further heteroatom, such as O, S, Se or Te, such as: aziridines, diaziridines, pyrroles, dihydropyrroles,

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tetrahydropyrroles, pyrazoles, dihydropyrazoles, tetrahydropyrazoles, imidazoles, dihydroimidazoles, tetrahydroimidazoles, dihydroimidazoles, 1,2,3-triazoles, 1,2,4-triazoles, tetrazoles, pentazoles, piperidines, pyridines, pyridazines, pyrimidines, pyrazines, piperazines, 1,2,3-triazines, 1,2,4-triazines, 1,2,3-triazines, tetrazines, azepines, oxazoles, isoxazoles, thiazoles, isothiazoles, thiadiazoles and morpholines, and benzofused derivatives thereof, such as: indoles, isoindoles, indolizines, indazoles, benzimidazoles, benzotriazoles, quinolines, isoquinolines, phthalazines, quinazolines, quinoxalines, phenazines, benzazepines, benzothiazoles and benzoxazoles.

Compounds which are likewise preferred are fused N-heterocyclic compounds, such as triazolo and tetrazolo compounds, which can contain at least one N-hydroxyl, oxime, N-oxy and N,N-dioxy function and, in addition to N, a further heteroatom, such as O, S, Se or Te.

[1,2,4] triazolo[4,3-a] pyridines
[1,2,4] triazolo[1,5-a] pyridines
[1,2,4] triazolo[4,3-a] quinolines
[1,2,4] triazolo[4,3-b] isoquinolines
[1,2,4] triazolo[3,4-a] isoquinolines
[1,2,4] triazolo[1,5-b] isoquinolines
[1,2,4] triazolo[5,1-a] isoquinolines

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[1,2,3] triazolo[1,5-a] pyridines
[1,2,3] triazolo[4,5-b] pyridines
[1,2,3] triazolo[4,5-c] pyridines
[1,2,3] triazolo[1,5-a] quinolines
[1,2,3] triazolo[5,1-a] isoquinolines
[1,2,4] triazolo[4,3-b] pyridazines
[1,2,4] triazolo[1,5-b] pyridazines
[1,2,4] triazolo[4,5-d] pyridazines
[1,2,4] triazolo[4,3-b] quinolines
[1,2,4] triazolo[3,4-a] phthalazines
[1,2,4] triazolo[4,3-a] pyrimidines
[1,2,4] triazolo[4,3-c] pyrimidines
[1,2,4] triazolo[1,5-a] pyrimidines
[1,2,4] triazolo[1,5-c] pyrimidines
[1,2,4] triazolo[4,3-c] quinazolines
[1,2,4] triazolo[1,5-a] quinazoline
[1,2,4] triazolo[1,5-c] quinazoline
[1,2,4] triazolo[5,1-b] quinazoline
[1,2,3] triazolo[1,5-a] pyrimidines
[1,2,3] triazolo[1,5-c] pyrimidines
[1,2,3] triazolo[4,5-d] pyrimidines
[1,2,3] triazolo[1,5-a] quinazolines
[1,2,3] triazolo[1,5-c] quinazolines
[1,2,4] triazolo[4,3-a] pyrazines

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[1,2,4] triazolo[1,5-a] pyrazines
[1,2,4] triazolo[1,5-a] pyrazines
[1,2,3] triazolo[4,5-b] pyrazines
[1,2,4] triazolo[4,3-a] quinoxalines
[1,2,3] triazolo[1,5-a] quinoxalines
[1,2,4] triazolo[4,3-b] [1,2,4] triazine
[1,2,4] triazolo[3,4-c] [1,2,4] triazine
[1,2,4] triazolo[4,3-d] [1,2,4] triazine
[1,2,4] triazolo[3,4-f] [1,2,4] triazine
[1,2,4] triazolo[1,5-b] [1,2,4] triazine
[1,2,4] triazolo[5,1-c] [1,2,4] triazine
[1,2,4] triazolo[1,5-d] [1,2,4] triazine
[1,2,4] triazolo[4,3-a] [1,3,5] triazine
[1,2,4] triazolo[1,5-a] [1,3,5] triazine
tetrazolo[1,5-a] pyridines
tetrazolo[1,5-b] isoquinolines
tetrazolo[1,5-a] quinolines
tetrazolo[5,1-a] isoquinolines
tetrazolo[1,5-b] pyridazines
tetrazolo[1,5-b] quinolines
tetrazolo[5,1-a] phthalazines
tetrazolo[1,5-a] pyrimidines
tetrazolo[1,5-c] pyrimidines
tetrazolo[1,5-a] quinazolines
tetrazolo[1,5-c] quinazolines

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tetrazolo[1,5-a] pyrazines
tetrazolo[1,5-a] quinoxalines
tetrazolo[1,5-b] [1,2,4] triazines
tetrazolo[5,1-c] [1,2,4] triazines
tetrazolo[1,5-d] [1,2,4] triazines
tetrazolo[5,1-f] [1,2,4] triazines

Others:

quinoline N-oxide
isoquinoline N-oxide
N-hydroxy-1,2,3,4-tetrahydro-isoquinoline
 β -(N-oxy-1,2,3,4-tetrahydroisoquinoline)-propionic acid
1,3-dihydroxy-2N-benzylimido-benzimidazoline

The multi-component system according to the invention:

(d) comprises, for example, aliphatic ethers or aryl-substituted alcohols, such as, for example,

2,3-dimethoxybenzyl alcohol
3,4-dimethoxybenzyl alcohol
2,4-dimethoxybenzyl alcohol
2,6-dimethoxybenzyl alcohol
homovanillyl alcohol
ethylene glycol monophenyl ether
2-hydroxybenzyl alcohol

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4-hydroxybenzyl alcohol
4-hydroxy-3-methoxybenzyl alcohol
2-methoxybenzyl alcohol
2,5-dimethoxybenzyl alcohol
3,4-dimethoxybenzylamine
2,4-dimethoxybenzylamine hydrochloride
veratryl alcohol
coniferyl alcohol
olefins (alkenes)
for example
2-allylphenol
2-allyl-6-methylphenol
allylbenzene
3,4-dimethoxypropenylbenzene
p-methoxystyrene
1-allylimidazole
1-vinylimidazole
styrene
stilbene
allyl phenyl ether
benzyl cinnamate
methyl cinnamate
2,4,6-triallyloxy-1,3,5-triazine
1,2,4-trivinylcyclohexane
4-allyl-1,2-dimethoxybenzene

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vinyl 4-tert-butylbenzoate

squalene

benzoin allyl ether

cyclohexane

dihydropyran

N-benzylcinnamanilide

preferably phenolic ethers, such as, for example

2,3-dimethoxybenzyl alcohol

3,4-dimethoxybenzyl alcohol

2,4-dimethoxybenzyl alcohol

2,6-dimethoxybenzyl alcohol

homovanillyl alcohol

4-hydroxybenzyl alcohol

4-hydroxy-3-methoxybenzyl alcohol

2-methoxybenzyl alcohol

2,5-dimethoxybenzyl alcohol

3,4-dimethoxybenzylamine

2,4-dimethoxybenzylamine hydrochloride

veratryl alcohol

coniferyl alcohol

veratrole

anisole

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preferably carbonyl compounds such as, for example,

4-aminobenzophenone

4-acetylbiphenyl

benzophenone

benzil

benzophenone hydrazone

3,4-dimethoxybenzaldehyde

3,4-dimethoxybenzoic acid

3,4-dimethoxybenzophenone

4-dimethylaminobenzaldehyde

4-acetylbiphenylhydrazone

benzophenone-4-carboxylic acid

benzoylacetone

bis-(4,4'-dimethylamino)-benzophenone

benzoin

benzoin oxime

N-benzoyl-N-phenylhydroxylamine

2-amino-5-chlorobenzophenone

3-hydroxy-4-methoxybenzaldehyde

4-methoxybenzaldehyde

anthraquinone-2-sulfonic acid

4-methylaminobenzaldehyde

benzaldehyde

benzophenone-2-carboxylic acid

3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

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(s)-(-)-2-(N-benzylpropyl)-aminobenzophenone
benzylphenylacetanilide
N-benzylbenzanilide
4,4'-bis-(diethylamino)-thiobenzophenone
4,4'-bis-(diacetylamino)-benzophenone
2-chlorobenzophenone
4,4'-dihydroxybenzophenone
2,4-dihydroxybenzophenone
3,5-dimethoxy-4-hydroxybenzaldehyde hydrazine
4-hydroxybenzophenone
2-hydroxy-4-methoxybenzophenone
4-methoxybenzophenone
3,4-dihydroxybenzophenone
p-anisic acid
p-anisaldehyde
3,4-dihydroxybenzaldehyde
3,4-dihydroxybenzoic acid
3,5-dimethoxy-4-hydroxybenzaldehyde
3,5-dimethoxy-4-hydroxybenzoic acid
4-hydroxybenzaldehyde
salicylaldehyde
vanillin
vanillic acid

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As a result of the addition of the compounds of the multi-component system mentioned under d) and e), the reaction is mediated in cascade form or the actual mediator compounds are recycled in situ, i.e. during the reaction, leading surprisingly to a substantial improvement in the kappa reduction or a reduction in the dose of mediator.

The additives mentioned under d) as defined above are preferably employed in amounts of 0.01 to 0.5 mg per g of lignin-containing material. 0.01 to 0.1 mg per g of lignin-containing material is particularly preferably employed.

The free amine of the particular mediator is preferably employed in a weight ratio of mediator/amine of 100:1 to 1:1, particularly preferably 20:1 to 1:1, especially preferably 10:1 to 2:1.

The activity of the multi-component system for modifying, degrading or bleaching of lignin, lignin-containing materials or similar substances is often increased further if Mg^{2+} ions are also present in addition to the constituents mentioned. The Mg^{2+} ions can be employed, for example, as a salt, such as, for example, $MgSO_4$. The concentration is in the range from 0.1 to 2 mg/g of lignin-containing material, preferably 0.2-0.6 mg/g.

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In some cases, a further increase in the activity of the multi-component system according to the invention can be achieved by the multi-component system also comprising, in addition to the Mg^{2+} ions, complexing agents, such as, for example, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentamethylenephosphonic acid (DTMPA), nitrilotriacetic acid (NTA), polyphosphoric acid (PPA) and the like. The concentration is in the range from 0.2 to 5 mg/g of lignin-containing material, preferably 1-3 mg/g.

The multi-component system according to the invention is used in a process for the treatment of lignin, for example, by mixing the components a) to e) as defined above selected in each case with an aqueous suspension of the lignin-containing material simultaneously or in any desired sequence.

A process using the multi-component system according to the invention is in the presence of oxygen or air under normal pressure up to 10 bar in a pH range from 2 to 11 at a temperature from 20°C to 95°C, preferably 40°C to 95°C, and a pulp consistency of 0.5% to 40% by weight is preferably carried out.

An unusual and surprising finding for the use of enzymes in bleaching pulp is that when the multi-component system

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according to the invention is employed, an increase in the pulp consistency results in a considerable increase in the kappa reduction which is possible.

Surprisingly, an increased pulp consistency thus leads to a better activity of the multi-component system.

A process according to the invention is preferably carried out at pulp consistencies of 12% to 15% by weight, particularly preferably of 14% to 15% by weight, for economic reasons.

Surprisingly, it has furthermore been found that an acid wash (pH 2 to 6, preferably pH 4 to 5) or Q stage (pH 2 to 6), preferably pH 4 to 5) before the enzyme mediator stage leads to a considerable reduction in kappa number in some pulps in comparison with treatment without this specific pretreatment. Chelating agents which are employed in the Q stage are the substances customary for this purpose (such as, for example EDTA or DTPA). They are preferably employed in concentrations of 0.1% to 1% by weight, particularly preferably 0.1% to 0.5% by weight.

100 to 100,000 IU of enzyme per g of lignin-containing material are preferably employed in the process according to the invention. 1,000 to 40,000 IU of enzyme per g of lignin-containing material are particularly preferred.

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0.01 mg to 100 mg of oxidizing agent per g of lignin-containing material are preferably employed in the process according to the invention. 0.01 to 50 mg of oxidizing agent per g of lignin-containing material are particularly preferably employed.

0.5 to 80 mg of mediator per g of lignin-containing material are preferably employed in the process according to the invention. 0.5 to 40 mg of mediator per g of lignin-containing material are particularly preferably employed.

By means of the multi-component system according to the invention, it has been possible, for example, to achieve the completely surprising result of a reduction in kappa number from about 30 to 10 within 1 to 4 hours in the bleaching of sulfate pulps (softwood), even at a high consistency in the region of about 15%, a considerable reduction in the concentration of component c) (mediator) being possible by addition of components d) and e) as defined above.

At the same time, reducing agents, which, together with the oxidizing agents present, serve to establish a particular redox potential, can be added.

Reducing agents which can be employed are sodium bisulfite, sodium dithionite, ascorbic acid, thio compounds, mercapto compounds of glutathione and the like.

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The reaction proceeds with the addition of oxygen or under an increased oxygen pressure in the case of laccase, and with hydrogen peroxide in the case of the peroxidases (for example lignin peroxidases or manganese peroxidases). The oxygen can also be generated here in situ, for example, by hydrogen peroxide + catalase, and the hydrogen peroxide can be generated in situ by glucose + GOD or other systems.

Agents which form free radicals or agents which trap free radicals (trapping of, for example, OH or OOH radicals) can furthermore be added to the system. These can improve the interaction between the redox and free radical mediators.

Other metal salts can also be added to the reaction solution.

These are important, in interaction with chelating agents, as agents which form free radicals or redox-centers. The salts form cations in the reaction solution. Such ions are, inter alia, Fe^{2+} , Fe^{3+} , Mn^{2+} , Mn^{3+} , Mn^{4+} , Cu^{2+} , Ca^{2+} , Ti^{3+} , Ce^{4+} and Al^{3+} .

The chelates present in the solution can furthermore serve as mimic substances for the enzymes, for example for the laccases (copper complexes) or for the lignin peroxidases or manganese peroxidases (heme complexes). Mimic substances are to be understood as

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those substances which simulate the prosthetic groups of (in this case) oxidoreductases and can catalyze, for example, oxidation reactions.

NaOCl can furthermore be added to the reaction mixture. This compound can form singlet oxygen by interaction with hydrogen peroxide.

Finally, it is also possible to operate with the use of detergents. Possible detergents are nonionic, anionic, cationic and amphoteric surfactants. The detergents can improve the penetration of the enzymes and mediators into the fiber.

It may likewise be necessary for the reaction to add polysaccharides and/or proteins. Polysaccharides which are to be mentioned here in particular are glucans, mannans, dextrans, levans, pectins, alginates or plant gums and/or intrinsic polysaccharides formed by the fungi or polysaccharides produced in the mixed culture with yeasts, and proteins which may be mentioned here in particular are gelatins and albumin.

These substances chiefly serve as protective colloids for the enzymes.

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Other proteins which can be added are proteases, such as pepsin, bromelin, papain and the like. These can serve, inter alia, to achieve better access to the lignin by degradation of the extensive C, a hydroxyproline-rich protein, present in the wood.

Other possible protective colloids are amino acids, simple sugars, oligomeric sugars, PEG types of the most diverse molecular weights, polyethylene oxides, polyethyleneimines and polydimethylsiloxanes.

The process according to the invention can be employed not only for delignification (bleaching) of sulfate, sulfite, organosolv or other pulps and of mechanical pulps, but also for the production of pulps generally, whether from woody or annulae plants, if defibrillation by the customary cooking processes (if necessary associated with mechanical processes or pressure), i.e. a very gentle cooking, to kappa numbers which can be in the range from about 50 to 120 kappa, is ensured.

For bleaching of pulps and also for the production of pulps, the treatment can be repeated several times, either after washing and extraction of the treated pulp with NaOH or without these intermediate steps. This leads to kappa values which are considerably lower still and to considerable increases in brightness. An O₂ stage can likewise be employed before the enzyme/ mediator treatment, or, as

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has already been mentioned, an acid washing or Q stage (chelating stage) can also be carried out.

In the "liquefaction" of coal (hard coal, brown coal), a similar process procedure as for delignification (bleaching) of wood or annual plant pulp is carried out.

Other objects and features of the present invention will become apparent from the following Examples, which disclose the preferred embodiments of the present invention. It should be understood, however, that the Examples are designed for the purpose of illustration only and not as a definition of the limits of the invention.

EXAMPLE 1/2

Example: Enzymatic bleaching of sulfate pulp.

Example 1:

30 g of dry weight pulp (softwood O₂ delignified), pulp consistency 30% (~ 100 g moist) are added to the following solutions:

- 1) 150 mg of hydroxybenzotriazole (HBT), 15 mg of benzotriazole (BT) and 3 mg of benzophenone (B) are added to 120 ml of tapwater, while stirring, and the pH is adjusted with 0.5 M H₂SO₄ such that pH 4.5 results after addition of the pulp and of the enzyme. 4,000 IU (1 IU = conversion of 1 μ M syringaldazine/minute/ml of

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enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. The solution is topped up to about 200 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

The pulp is then introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in the range of 1-10 bar for 1-4 hours.

Thereafter, the pulp is washed over a nylon screen (30 µm) and extracted for 1 hour at 60°C at a pulp consistency of 8% with 2% of NaOH per g of pulp.

After renewed washing of the pulp, the kappa number is determined.

(see Table 1)

(see Table 2)

Modifications for Example/Table 2:

with 75 mg of hydroxybenzotriazole, 7.5 mg of benzotriazole and 0.02 mg of veratryl alcohol.

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EXAMPLE 1

Example: Enzymatic bleaching of sulfate pulp.

30 g of dry weight pulp (softwood), pulp consistency 30% (- 100 g moist) are added to the following solution:

60 mg of DTPA and 15 mg of $MgSO_4$ are added to 120 ml of tapwater, while stirring. The pH is adjusted with 0.5 M H_2SO_4 such that pH 4.5 results after addition of the pulp and of the enzyme. 4,000 IU (1 IU = conversion of 1 μM syringaldazine/minute/ml of enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. The solution is topped up to about 200 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

Thereafter, the pulp is introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in a range of 1-10 bar for 1-4 hours.

The pulp is then washed over a nylon screen (30 μm) and extracted for 1 hour at 60°C at a pulp consistency of 8% with 2% of NaOH per g of pulp.

After renewed washing of the pulp, the kappa number is determined.

The results are reported in Table 3.

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EXAMPLE 4

Example: Enzymatic bleaching of sulfate pulps with a prior Q stage.

30 g of dry weight pulp (softwood 1 and softwood 2), pulp consistency 30% (- 100 g moist) are added to the following solutions:

1) Q stage: 90 mg of DTPA are added to 120 ml of tapwater and the pH is adjusted with 0.5 M H_2SO_4 such that pH 4.5 results after addition of the pulp. The solution is topped up to about 200 ml and mixed with a dough kneader for 2 minutes.

The pulp is then left in a closed glass beaker at 90°C.

It is then washed thoroughly (tapwater), and the pulp is brought to a pulp consistency of 30% and added to the following solution:

2) Laccase/extraction stage: 300 mg of hydroxybenzotriazole are added to 120 ml of tapwater, while stirring. The pH is adjusted with 0.5 M H_2SO_4 such that pH 4.5 results after addition of the pulp and of the enzyme. 4,000 IU (1 IU = conversion of 1 μ M syringaldazine/minute/ml of enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. The solution is topped up to about 260 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

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Thereafter, the pulp is introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in the range of 1-10 bar for 1-4 hours.

Thereafter, the pulp is washed over a nylon screen (30 μ m) and extracted for 1 hour at 60°C at a pulp consistency of 8% with 2% of NaOH per g of pulp.

After renewed washing of the pulp, the kappa number is determined. The kappa number after the Q stage is determined in parallel batches. The results are reported in Table 4.

EXAMPLE 5

Example: Enzymatic bleaching and sulfate pulp.

30 g of dry weight pulp (softwood 1/softwood 2), pulp consistency 30% (~ 100 g moist) are added to the following solutions:

300 mg of hydroxybenzotriazole (softwood 1) and 150 or 300 mg of hydroxybenzotriazole (softwood 2) are added to 120 ml of tapwater, while stirring, and the pH is adjusted with 0.5 M H_2SO_4 , such that pH 4.5 results after addition of the pulp and of the enzyme. 4,000 IU (1 IU = conversion of 1 μ M syringaldazine/minute/ml of enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. The solution is topped up to 200 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

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At a pulp consistency of 15%, 30 g of bone dry = 100 g of moist pulp are added to 200 g of the total amount, i.e. 80 ml of tapwater are taken and are topped up to 100 ml. The procedure is otherwise as for a 10% pulp consistency.

Thereafter, the pulp is introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in the range of 1-10 bar for 1-4 hours.

Thereafter, the pulp is washed over a nylon screen (30 μ m) and extracted for 1 hour at 60°C at a pulp consistency of 3% with 2% of NaOH per g of pulp.

After renewed washing of the pulp, the kappa number is determined.

The results are reported in table 5.

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EXAMPLES/TABLES:

EXAMPLE 1

Enzymatic bleaching of sulfate pulp (softwood) (O₂ delignified)

TABLE 1

<u>System</u>	<u>Kappa before Extraction</u>	<u>Kappa after Extraction</u>	<u>Lignin Degradation %</u>
1) 0 value	11	10	9.1
2) L+5 mg of HBT/g	7.5	5.2	47.3
3) L+5 mg of HBT/g +BT/B	6.9	4.9	54.5
4) L+5 mg of HBT/g		8.5	22.8
5) L+5 mg of HBT/g +BT/B		6.1	44.6
2.)3.) under a pressure of 10 bar			
4.)5.) air			
B = benzophenone			
L = laccase			

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EXAMPLE 2

Enzymatic bleaching of sulfate pulp (softwood) (G, delignified)

TABLE 1

<u>System</u>	<u>Kappa before Extraction</u>	<u>Kappa after Extraction</u>	<u>Lignin Degradation %</u>
0 value	21	18	9.1
L+2.5 mg of HBT/g	8.5	7.8	31
L+2.5 mg of HBT/g			
+BT/VA	8.1	6.4	42

VA = veratryl alcohol

L = laccase

EXAMPLE 3

Enzymatic bleaching of sulfate pulp (softwood)

TABLE 2

<u>System</u>	<u>Kappa before Extraction</u>	<u>Kappa after Extraction</u>	<u>Lignin Degradation</u>
0 value	28.7	25.8	6.7
L+10 mg of HBT/g	21	17.8	33.2
L+10 mg of HBT/g			
+ (A)	19.1	14.9	43.2

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(A) - 2 mg. of DTFA/g of pulp
8.5 mg of H_2SO_4 /g of pulp

L. - Laccase

TABLE 4

TABLE 3

Sample	Kappa before O ₂	Kappa after O ₂	Kappa before oxidation	Kappa after oxidation	Kappa after O ₂
Sample SW 1	22	21.5	28	24.4	22.4
1.0 mg of SW 1	28		24.5	17.8	
1.0 mg of SW 1	28	21.5	18.8	14.8	
Sample SW 2	22.7	21.8	22.7	21.5	21.8
1.0 mg of SW 2	22.7		21.9	16.4	
1.0 mg of SW 2	22.7	21.3	18.1	14.4	

L. - Laccase

Sample SW 1

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SW1: 37.2% without Q and 47.2% with Q

SW2: 27.8% without Q and 38.6% with Q

EXAMPLE 5

TABLE 5

<u>System</u>	<u>Kappa before extraction</u>	<u>Kappa after extraction</u>	<u>Pulp con- sistency</u>	<u>Lignin removal %</u>
0 value SW 1	28.7	26.8		66
10 mg of HBT/g				
SW 1	21	17.8	10	38
10 mg of HBT/g				
SW 1	18.9	14.8	15	47.7
0 value SW 2	15	14.1		6
5 mg of HBT/g				
SW 2	10.1	7.2	10	52
5 mg of HBT/g				
SW 2	7.8	5.4	15	64
10 mg of HBT/g				
SW 2	7	5.1	10	66

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EXAMPLE 4

Example: Enzymatic bleaching of sulfate pulp.

30 g of dry weight pulp (softwood 0, delignified), pulp consistency 30% (- 100 g moist) are added to the following solutions:

- 1) 300 mg of hydroxybenzotriazole are added to 120 ml of tapwater, while stirring, and the pH is adjusted with 0.5 M H_2SO_4 , such that pH 4.5 results after addition of the pulp and of the enzyme. 1000 or 10,000 IU (IU = conversion of 1 μM of syringaldazine/minute/ml of enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. 1000 IU of ligninperoxidase/g of pulp, 1000 IU of peroxidase (horseradish)/g of pulp and 1000 IU of tyrosinase/g of pulp are added in each case in separate batches. The solution is topped up to about 200 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

Thereafter, the pulp is introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in the range of 1-10 bar for 1-4 hours.

The pulp is then washed over a nylon screen (30 μm) and extracted for 1 hour at 60°C at a pulp consistency of 8% with 2% of NaOH per g of pulp.

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After renewed washing of the pulp, the kappa number is determined. (see Table 6).

TABLE 6

<u>Enzymes</u>	<u>Kappa (pulp)</u>	
	<u>before treatment</u>	<u>after treatment</u>
Lignin peroxidase	15.2	11.3
Peroxidase (horseradish)		
19036 Serva	15.2	11.75
Tyrosinase		
T-7753 Sigma	15.2	11.35
Laccase 10000 IU	15.2	5.5
Laccase 1000 IU	15.2	10.0

EXAMPLE 7

Example: Enzymatic bleaching of sulfate pulp.

30 g of dry weight pulp (softwood/hardwood), pulp consistency 30% (- 100 g moist) are added to the following solutions:

- 1) 300 mg of hydroxybenzotriazole are added to 120 ml of tapwater, while stirring, and the pH is adjusted with 0.5 M H₂SO₄ such that pH 4.5 results after addition of the pulp and of the enzyme.
20000 IU (IU = conversion of 1 µM of syringaldazine/minute/ml of

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enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. The solution is topped up to about 200 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

Thereafter, the pulp is introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in the range of 1-10 bar for 1-4 hours.

The pulp is then washed over a nylon screen (30 µm) and extracted for 1 hour at 60°C at a pulp consistency of 8% with 2% of NaOH per g of pulp.

After renewed washing of the pulp, the kappa number is determined.

A kappa number reduction from 15 to 6 in the case of hardwood and from 30 to 15 in the case of softwood was achieved.

EXAMPLE 8

Example: Enzymatic bleaching of straw pulp.

30 g of dry weight straw pulp, pulp consistency 30% (- 100 g moist) are added to the following solutions:

- 1) 300 mg of hydroxybenzotriazole are added to 120 ml of tapwater, while stirring, and the pH is adjusted with 0.3 M H_2SO_4 , such

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that pH 4.5 results after addition of the pulp and of the enzyme. 20000 IU (IU = conversion of 1 μ M of syringaldazine/minute/ml of enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. The solution is topped up to about 200 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

Thereafter, the pulp is introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in the range of 1-10 bar for 1-4 hours.

The pulp is then washed over a nylon screen (30 μ m) and extracted for 1 hour at 60°C at a pulp consistency of 8% with 2% of NaOH per g of pulp.

After renewed washing of the pulp, the kappa number is determined.

A reduction in the kappa number from 65 to 14 was achieved.

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EXAMPLE 9

Example: Enzymatic bleaching of sulfite pulp.

30 g of dry weight pulp (sulfite pulp), pulp consistency 30% (- 100 g moist) are added to the following solutions:

1) 300 mg of hydroxybenzotriazole are added to 120 ml of tapwater, while stirring, and the pH is adjusted with 0.5 M H_2SO_4 such that pH 4.5 results after addition of the pulp and of the enzyme. 20000 IU (IU = conversion of 1 μM of syringaldazine/minute/ml of enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. The solution is topped up to about 200 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

Thereafter, the pulp is introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in the range of 1-10 bar for 1-4 hours.

The pulp is then washed over a nylon screen (30 μm) and extracted for 1 hour at 60°C at a pulp consistency of 8% with 2% of NaOH per g of pulp.

After renewed washing of the pulp, the kappa number is determined.

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A reduction in the kappa number from 15.5 to 5.2 was achieved.

EXAMPLE 10

Enzymatic bleaching of sulfate pulp (softwood/O₂ delignified/hardwood (2-fold treatment))

30 g of dry weight pulp (hardwood or softwood), pulp consistency 30% (~ 100 g moist) are added to the following solutions:

1) 300 mg of hydroxybenzotriazole are added to 120 ml of tapwater, while stirring, and the pH is adjusted with 0.5 M H₂SO₄ such that pH 4.5 results after addition of the pulp and of the enzyme. 20000 IU (IU = conversion of 1 μ M of syringaldazine/minute/ml of enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. The solution is topped up to about 200 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

Thereafter, the pulp is introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in the range of 1-10 bar for 1-4 hours.

The pulp is then washed over a nylon screen (30 μ m) and extracted for 1 hour at 60°C at a pulp consistency of 8% with 2% of NaOH per g of pulp.

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a) Directly after the incubation, enzyme + mediator are added, without washing step, the mixture is mixed (2 minutes) and the reaction is carried out again (same dosage as the first treatment).

b) Directly after the incubation, after the washing step and pressing out of the pulp to a pulp consistency of 30%, the reaction, is carried out again by adding all the components.

c) After incubation, after washing of the pulp, and after extraction and renewed washing and pressing out of the pulp to a pulp consistency of 30%, the reaction is carried out again by adding all the components:

Hardwood	Softwood:
reduction in kappa number	reduction in kappa number
a) 15 to 5	a) 15.5 to 4.2
b) 15 to 3.5	b) 15.5 to 3
c) 15 to 2.5	c) 15.2 to 2.2

EXAMPLE 11

Example: Enzymatic bleaching of mechanical wood pulp

30 g of dry weight mechanical wood pulp (spruce), pulp consistency 30% (- 100 g moist) are added to the following solutions:

- 1) 300 mg of N-hydroxyhexahydroazepine are added to 120 ml of tapwater, while stirring, and the pH is adjusted with 0.5 M H_2SO_4 .

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such that pH 4.5 results after addition of the pulp and of the enzyme. 1000 IU (IU = conversion of 1 μ M of syringaldazine/minute/ml of enzyme) of laccase from *Coriolus versicolor* are added per g of pulp. The solution is topped up to about 200 ml and the pulp is added. The mixture is mixed with a dough kneader for 2 minutes.

Thereafter, the pulp is introduced into a reaction bomb preheated to 45°C and is incubated under a pressure in the range of 1-10 bar for 1-4 hours.

The pulp is then washed over a nylon screen (30 μ m).

An increase in brightness of 7% ISO was achieved.

While only a single embodiment of the present invention has been shown and described, it is to be understood that many changes and modifications may be made thereunto without departing from the spirit and scope of the invention as defined in the appended claims.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A system for modifying, degrading or bleaching
lignin, lignin-containing materials or similar substances, which
comprises, as a multi-component system,

(a) if appropriate at least one oxidation
catalyst;

(b) at least one suitable oxidizing agent;

(c) at least one mediator selected from the group
consisting of hydroxylamines, hydroxylamine derivatives, hydroxamic
acids, hydroxamic acid derivatives and aliphatic, cycloaliphatic,
heterocyclic or aromatic compounds which contain at least one N-
hydroxy, oxime, N-oxy, or N,N' dioxy function;

(d) if appropriate, at least one comediator
selected from the group consisting of aryl-substituted alcohols,
carbonyl compounds, aliphatic ethers, phenolic ethers olefins
(alkenes) and the mixtures thereof; and

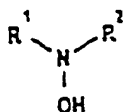
(e) a small amount of at least one free amine of a
mediator employed in each case.

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2. A multi-component system as claimed in claim 1, further comprising Mg^{2+} ions, in addition to the components (a) to (e).
3. A multi-component system as claimed in claim 1, wherein an oxidation catalyst is employed, and said oxidation catalyst comprises an oxidoreductase of classes 1.1.1 - 1.97.
4. A multi-component system as claimed in claim 3, in which an oxidoreductase which uses oxygen, peroxide or quinone as an electron acceptor is employed.
5. A multi-component system as claimed in claim 3, in which laccase (1.10.3.2) is employed as the oxidoreductase.
6. A multi-component system as claimed in claim 1, in which an N-hydroxyl, oxime, N-oxy, or N,N'-dioxy compound or hydroxyamic acid derivative in a one-component or multi-component system is employed as the NO-, NOH- or H-NR-OH-containing aliphatic, cycloaliphatic, heterocyclic or aromatic compound.

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7. A multi-component system as claimed in claim 6,
in which as the NO-, NOH- or H-NR-OH containing
compounds a hydroxylamine of the general formula I is employed



I

in which, in the general formula I, the substituents R¹ and R², which
can be identical or different, independently of one another are one of
the following groups: hydrogen, C₁-C₁₂-alkyl, carbonyl-C₁-C₆-alkyl,
phenyl or aryl, the C₁-C₁₂-alkyl, carbonyl-C₁-C₆-alkyl, phenyl or aryl,
of which can be unsubstituted or furthermore mono- or polysubstituted
by the radical R³, and

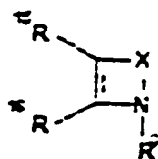
in which the radical R³ can be one of the
following groups: hydrogen, halogen, hydroxyl, foraryl, carboxyl and
salts and esters thereof, amino, nitro, C₁-C₁₂-alkyl, C₁-C₆-alkoxy,
carbonyl-C₁-C₆-alkyl, phenyl, sulfono, esters and salts thereof,
sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and salts and
esters thereof, in which the amino, carbamoyl and sulfamoyl groups of
the radical R³ furthermore can be unsubstituted or mono- or
disubstituted by hydroxyl, C₁-C₆-alkyl or C₁-C₆-alkoxy, and

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in which the radicals R^1 and R^2 together can form a group -B-, and -B- is one of the following groups: $(-CHR^1-)_n$, or $(-CR^1=CH-)_n$, and in which R^1 is a substituent which is defined as R^1 , and n is an integer from 1 to 6 and m is an integer from 1 to 1.

8. A multi-component system as claimed in claim 4.

wherein as the NO-, NOH-, or HNR-OH-containing compounds a substance of the general formula II is employed



in which X is one of the following groups: $(-N=N-)$, $(-N=CR^{10}-)$, $(-CR^{10}=N-)$, $(-CR^{11}=CR^{12}-)$,



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and p is 1 or 2,

in which the radicals R^1 to R^p , R^q and R^s can be identical or different and independently of one another are one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, sulfonyl, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and salts and esters thereof, and in which the amino, carbamoyl and sulfamoyl groups of the radicals R^1 to R^p , R^q and R^s furthermore can be unsubstituted or mono- or disubstituted by hydroxyl, C_1-C_6 -alkyl, C_1-C_6 -alkoxy, and

in which the radicals R^q and R^s can form a common group -G- and -G- is one of the following groups:

$(-CR^1-CR^2-CR^3-CR^4-)$ or $(-CR^1-CR^2-CR^3-CR^4-)$;

the radicals R^1 to R^4 can be identical or different and independently of one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, sulfonyl, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and salts and esters thereof, and in which the amino, carbamoyl and sulfamoyl groups of the radicals R^1 to R^4 furthermore can be unsubstituted or mono- or disubstituted by hydroxyl, C_1-C_6 -alkyl or C_1-C_6 -alkoxy, and in which the C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy,

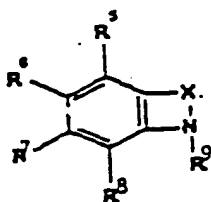
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carbonyl-C₁-C₆-alkyl, phenyl and aryl groups of the radicals R¹ and R² can be unsubstituted or furthermore mono- or polysubstituted by the radical R¹¹, and

in which the radical R¹¹ is one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C₁-C₁₂-alkyl, C₁-C₆-alkyloxy, carbonyl-C₁-C₆-alkyl, phenyl, aryl, and esters and salts thereof, and

in which the carbamoyl, sulfamoyl and amino groups of the radical R¹¹ can be unsubstituted or furthermore mono- or disubstituted by the radical R¹², and in which the radical R¹² can be one of the following groups: hydrogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C₁-C₁₂-alkyl, C₁-C₆-alkyloxy, carbonyl-C₁-C₆-alkyl, phenyl and aryl.

9. A multi-component system as claimed in claim 6, as the NO-, NOH-, or H-NR-OH-containing compounds wherein a substance of the general formula III is employed



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in which X is one of the following groups: $(-N-E-)$,

$(-N=CR^{10}-)$, $(-CR^{10}=N-)$, $(-CR^{11}=CR^{12}-)$,



and p is 1 or 2;

the radicals R^1 to R^{12} can be identical or different and independently of one another are one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, aryl, sulfono, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and salts and esters thereof, and the amino, carbamoyl and sulfamoyl groups thereof can furthermore be unsubstituted or mono- or disubstituted by hydroxyl, C_1-C_6 -alkyl or C_1-C_6 -alkoxy, and in which the C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl and aryl and aryl- C_1-C_6 -alkyl groups of the radicals R^1 to R^{12} can be unsubstituted or furthermore mono- or polysubstituted by the radical R^{13} , and

in which the radical R^{13} can be one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, aryl, sulfono, sulfeno, sulfinio and

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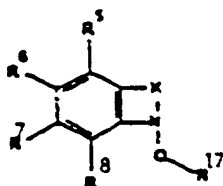
esters, and in which the carbamoyl, sulfamoyl, and amino groups of the radical R^{13} can be unsubstituted or furthermore mono- or disubstituted by the radical R^{14} , and

in which the radical R^{14} can be one of the following groups: hydrogen, hydroxyl, formyl, carboxyl and salts and ester thereof, amino, nitro, C_1-C_{12} -alkyl, C_1-C_6 -alkyloxy, carbonyl- C_1-C_6 -alkyl, phenyl, or aryl.

10. A multi-component system as claimed in claim

6,

wherein as the NO-, NOH- or H-NR-OH-containing compounds a substance of the general formula IV is employed



IV

in which X is one of the following groups: $(-N=N-)$, $(-N=CR^{18}-)$, $(-CR^{18}=N-)$, $(-CR^{18}=CR^{19}-)$,



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an p is 1 or 2;

the above statements apply to the radicals R¹ to R⁶

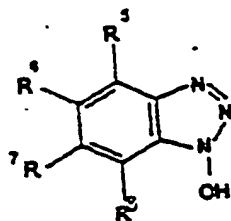
and R¹⁰ to R¹²;

R¹⁷ can be: hydrogen, C₁-C₁₀-alkyl or C₁-C₁₀-alkyl-carbonyl, the C₁-C₁₀-alkyl and C₁-C₁₀-alkylcarbonyl of which can be unsubstituted or mono- or polysubstituted by a radical R¹⁸, which is defined as R³.

11. A multi-component system as claimed in claim

6,

wherein as the NO-, NOH- or H-NR-OH-containing compounds a 1-hydroxybenzotriazole or tautomeric benzotriazole 1-oxide or ester or salt thereof according to the following formula V is employed



V

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in which the radicals R^1 to R^4 can be identical or different and independently of one another are one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_n -alkyl, C_1-C_n -alkyloxy, carbonyl- C_1-C_n -alkyl, phenyl, sulfono, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and salts and esters thereof, and in which the amino, carbamoyl and sulfamoyl groups of the radicals R^1 to R^4 furthermore can be unsubstituted or mono- or disubstituted by hydroxyl, C_1-C_n -alkyl or C_1-C_n -alkoxy, and in which the C_1-C_n -alkyl, C_1-C_n -alkyloxy, carbonyl- C_1-C_n -alkyl, phenyl and aryl groups of the radicals R^1 to R^4 can be unsubstituted or furthermore mono- or polysubstituted by the radical R'' , and

in which the radical R'' can be one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_n -alkyl, C_1-C_n -alkyloxy, carbonyl- C_1-C_n -alkyl, phenyl, aryl, sulfono, sulfeno, sulfinio and esters thereof, and in which the carbamoyl, sulfamoyl and amino groups of the radical R'' can be unsubstituted or furthermore mono- or disubstituted by the radical R''' , and

in which the radical R''' can be one of the following groups: hydrogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C_1-C_n -alkyl, C_1-C_n -alkyloxy,

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carbonyl-C₁-C₂-alkyl, phenyl, and aryl,

12. A multi-component system as claimed in claim 6,

wherein the NO-, NOH-, or H-NR-OH-containing compound employed is one chosen from azoles.

13. A multi-component system as claimed in claim 6,

wherein the NO-, NOH-, or H-NR-OH-containing compound employed is one chosen from condensed heterocyclic compounds which contain a triazolo or tetrazolo unit, and is selected from the group consisting of:

[1,2,4] triazolo [4,3-a] pyridines,
[1,2,4] triazolo [1,5-a] pyridines,
[1,2,4] triazolo [4,3-a] quinolines,
[1,2,4] triazolo [4,3-b] isoquinolines,
[1,2,4] triazolo [3,4-a] isoquinolines,
[1,2,4] triazolo [1,5-b] isoquinolines,
[1,2,3] triazolo [5,1-a] isoquinolines,
[1,2,3] triazolo [1,5-a] pyridines,

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[1,2,3] triazolo [4,5-b] pyridines,
[1,2,3] triazolo [4,5-c] pyridines,
[1,2,3] triazolo [1,5-a] quinolines,
[1,2,3] triazolo [5,1-a] isoquinolines,
[1,2,4] triazolo [4,3-b] pyridazines,
[1,2,4] triazolo [1,5-b] pyridazines,
[1,2,4] triazolo [4,5-d] pyridazines,
[1,2,4] triazolo [4,3-b] quinolines,
[1,2,4] triazolo [3,4-a] phthalazines,
[1,2,4] triazolo [4,3-a] pyrimidines,
[1,2,4] triazolo [4,3-c] pyrimidines,
[1,2,4] triazolo [1,5-a] pyrimidines,
[1,2,4] triazolo [1,5-c] pyrimidines,
[1,2,4] triazolo [4,3-c] quinazolines,
[1,2,4] triazolo [1,5-a] quinazoline,
[1,2,4] triazolo [1,5-c] quinazoline,
[1,2,4] triazolo [5,1-b] quinazoline,
[1,2,3] triazolo [1,5-a] pyrimidines,
[1,2,3] triazolo [1,5-c] pyrimidines,
[1,2,3] triazolo [4,5-d] pyrimidines,
[1,2,3] triazolo [1,5-a] quinazolines,
[1,2,3] triazolo [1,5-c] quinazolines,
[1,2,4] triazolo [4,3-a] pyrazines,
[1,2,4] triazolo [1,5-a] pyrazines,
[1,2,4] triazolo [1,5-a] pyrazines,

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[1,2,3] triazolo [4,5-b] pyrazine,
[1,2,4] triazolo [4,3-a] quinoxalines,
[1,2,3] triazolo [1,5-a] quinoxalines,
[1,2,4] triazolo [4,3-b] [1,2,4] triazine,
[1,2,4] triazolo [3,4-c] [1,2,4] triazine,
[1,2,4] triazolo [4,3-d] [1,2,4] triazine,
[1,2,4] triazolo [3,4-f] [1,2,4] triazine,
[1,2,4] triazolo [1,5-b] [1,2,4] triazine,
[1,2,4] triazolo [5,1-c] [1,2,4] triazine,
[1,2,4] triazolo [1,5-d] [1,2,4] triazine,
[1,2,4] triazolo [4,3-a] [1,3,5] triazine,
[1,2,4] triazolo [1,5-a] [1,3,5] triazine,
tetrazolo [1,5-a] pyridines,
tetrazolo [1,5-b] isoquinolines,
tetrazolo [1,5-a] quinolines,
tetrazolo [5,1-a] isoquinolines,
tetrazolo [1,5-b] pyridazines,
tetrazolo [1,5-b] quinolines,
tetrazolo [5,1-a] phthalazines,
tetrazolo [1,5-a] pyrimidines,
tetrazolo [1,5-c] pyrimidines,
tetrazolo [1,5-a] quinazolines,
tetrazolo [1,5-c] quinazolines,
tetrazolo [1,5-a] pyrazines,
tetrazolo [1,5-a] quinoxalines.

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tetrazolo [1,5-b] [1,2,4] triazines,
tetrazolo [5,1-c] [1,2,4] triazines,
tetrazolo [1,5-d] [1,2,4] triazines, and
tetrazolo [5,1-f] [1,2,4] triazines.

14. A multi-component system as claimed in claim 1,

wherein the oxidizing agent employed is selected from the group consisting of air, oxygen, ozone, H_2O_2 , an organic peroxide, a peracid as for example, peracetic acid, performic acid, persulfuric acid, pernitric acid, metachloroperoxybenzoic acid, perchloric acid, perchlorate, peracetate, persulfate, other peroxide, an oxygen species, a free radical as OH ; OOH ; superoxide ($O_2^{\cdot-}$), singlet oxygen, ozone, ozonide, the dioxygenylation ($O_2^{\cdot+}$), a dioxirane, a dioxetane and a Fremy radical.

15. A multi-component system as claimed in claim 1,

in which the compound of component (d) is an aliphatic ether or aryl-substituted alcohol selected from the group consisting of:

2,3-dimethoxybenzyl alcohol,
3,4-dimethoxybenzyl alcohol,
2,4-dimethoxybenzyl alcohol.

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2,6-dimethoxybenzyl alcohol,
homovanillyl alcohol,
ethylene glycol monophenyl ether,
2-hydroxybenzyl alcohol,
4-hydroxybenzyl alcohol,
4-hydroxybenzyl-3-methoxybenzyl alcohol,
2-methoxybenzyl alcohol,
2,3-dimethoxybenzyl alcohol,
3,4-dimethoxybenzylamine,
2,4-dimethoxybenzylamine hydrochloride,
veratryl alcohol, and
coniferyl alcohol.

16. A multi-component system as claimed in claim 1,

wherein the compound of component (d) is an olefin
(alkene) selected from the group consisting of:

2-allylphenol,
2-allyl-6-methylphenol,
allylbenzene,
3,4-dimethoxypropenylbenzene,
p-methoxystyrene,
1-allylimidazole,
1-vinylimidazole,

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styrene,
stilbene,
allyl phenyl ether,
benzyl cinnamate,
methyl cinnamate,
2,4,6-triallyloxy-1,3,5-triazine,
1,2,4-trivinylcyclohexane,
4-allyl-1,2-dimethoxybenzene,
vinyl 4-tert-butylbenzoate,
squalene,
benzoin allyl ether,
cyclohexene,
dihdropyran, and
N-benzylcinnamamide.

17. A multi-component system as claimed in claim 1,

wherein the compound of component (d) is a
phenolic ether selected from the group consisting of

2,3-dimethoxybenzyl alcohol,
3,4-dimethoxybenzyl alcohol,
2,4-dimethoxybenzyl alcohol,
2,6-dimethoxybenzyl alcohol,
homovanillyl alcohol,

4-acetylbiphenylhydrazones,
 benzophenone-4-carboxylic acid,
 benzoylacetone,
 bis-(4,4'-dimethylamino)-benzophenone,
 benzoin,
 benzoin oxime,
 N-benzoyl-N-phenylhydroxylamine,
 2-amino-5-chlorobenzophenone,
 3-hydroxy-4-methoxybenzaldehyde,
 4-methoxybenzaldehyde,
 anthraquinone-2-sulfonic acid,
 4-methylaminobenzaldehyde,
 benzaldehyde,
 benzophenone-2-carboxylic acid,
 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride,
 (S)-(-)-2-(N-benzylpropyl)-amino benzophenone,
 benzylphenylacetanilide,
 N-benzylbenzanilide,
 4,4'-bis-(dimethylamino)-thiobenzophenone,
 4,4'-bis-(diacetylamino)-benzophenone,
 2-chlorobenzophenone,
 4,4'-dihydroxybenzophenone,
 2,4-dihydroxybenzophenone,
 3,5-dimethoxy-4-hydroxybenzaldehyde hydrazone,
 4-hydroxybenzophenone,

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4-acetylbiphenylhydrazone,
benzophenone-4-carboxylic acid,
benzoylacetone,
bis-(4,4'-diethylamino)-benzophenone,
benzoin,
benzoin oxime,
N-benzoyl-N-phenylhydroxylamine,
2-amino-5-chlorobenzophenone,
3-hydroxy-4-methoxybenzaldehyde,
4-methoxybenzaldehyde,
anthraquinone-2-sulfonic acid,
4-methylaminobenzaldehyde,
benzaldehyde,
benzophenone-2-carboxylic acid,
3,3',4,4'-benzophenonetetracarboxylic acid dianhydride,
(S)-(-)-2-(N-benzylpropyl)-aminobenzophenone,
benzylphenylacetanilide,
N-benzylbenzanilide,
4,4'-bis-(diethylamino)-thiobenzophenone,
4,4'-bis-(diacetylamino)-benzophenone,
2-chlorobenzophenone,
4,4'-dihydroxybenzophenone,
2,4-dihydroxybenzophenone,
3,5-dimethoxy-4-hydroxybenzaldehyde hydrazine,
4-hydroxybenzophenone,

2-hydroxy-4-methoxybenzophenone,
 4-methoxybenzophenone,
 3,4-dihydroxybenzophenone,
 p-anisal acid,
 p-anisaldehyde,
 3,4-dihydroxybenzaldehyde,
 3,4-dihydroxybenzoic acid,
 3,4-dimethoxy-4-hydroxybenzaldehyde,
 3,5-dimethoxy-4-hydroxybenzoic acid,
 4-hydroxybenzaldehyde,
 salicylaldehyde,
 vanilla, and
 vanillic acid.

19. A multi-component system as claimed in claim 1,

wherein benzotriazole is employed as component (c)
 as a free amine in the case of in situ generation or mediation of the
 reaction in cyclic form in the case of hydroxybenzotriazole.

20. A process for softening, degrading or bleaching
 lignin, lignin-containing materials or similar substances, which
 comprises

mixing the components (a) to (e) as follows:

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(a) if appropriate at least one oxidation catalyst;

(b) at least one suitable oxidizing agent;

(c) at least one mediator selected from the group consisting of hydroxylamines, hydroxylamine derivatives, hydroxamic acids, hydroxamic acid derivatives and aliphatic, cycloaliphatic, heterocyclic or aromatic compounds which contain at least one N-hydroxy, oxime, N-oxy, or N,N' dioxy function;

(d) if appropriate, at least one comediator selected from the group consisting of aryl-substituted alcohols, carbonyl compounds, aliphatic ethers, phenolic ethers olefins (alkenes) and the mixtures thereof; and

(e) a small amount of at least one free amine of a mediator employed in each case; and

selected in each case with an aqueous suspension of the lignin-containing material simultaneously or in any desired sequence.

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21. The process as claimed in claim 20,

wherein the reaction is carried out in a pH range from 2 to 11 at a temperature from 20°C to 95°C, at a pulp consistency of 0.5% to 40% by weight under air or oxygen under normal pressure or 1-10 bar.

22. The process as claimed in claim 21,

wherein the temperature is 40°C to 95°C; and

wherein the pulp consistency is 1% to 15% by weight.

23. The process as claimed in claim 20, comprising

employing an acid wash or O stage before the reaction.

24. The process as claimed in claim 23, comprising

carrying out the acid wash at 60°C to 100°C at pH 4-5.5 for 10-90 minutes at a pulp consistency of 4% to 20% by weight.

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25. The process as claimed in claim 23, comprising

carrying out the Q stage with 0.05% - 1.0%, by weight of chelating agent at 60°C to 100°C at pH 4-5.5 for 10-90 minutes at a pulp consistency of 4% - 20% by weight.

26. The process as claimed in claim 23, comprising

maintaining acid wash conditions of 1 hour, at 90°C at pH 4-5.5 and a pulp consistency of 10% by weight.

27. The process as claimed in claim 20, comprising

adding to the reaction mixture, an enzyme selected from the group consisting of a hemicellulase, cellulase, amylase, pectinase, lipase and a mixture comprising two or more of said enzymes.

28. The process as claimed in claim 20,

wherein a modified enzyme, enzyme constituent, prosthetic group, zinc substance, a heme group or a compound containing heme groups, is employed.

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29. The process as claimed in claim 20,
wherein in addition to these substances, a phenolic compound and/or non-phenolic compound having one or more benzene nuclei is employed.
30. The process as claimed in claim 20, comprising adding a reducing agent to the reaction solution.
31. The process as claimed in claim 30,
wherein sodium bisulfite, sodium dithionite, ascorbic acid, a thiol compound, a mercapto compound or glutathione is employed as the reducing agent.
32. The process as claimed in claim 20,
wherein oxygen is generated in situ by H_2O_2 + catalase or H_2O_2 is generated in situ by GOD + glucose.
33. The process as claimed in claim 20,
wherein a cation-forming metal salt is added to the reduction solution.

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34. The process as claimed in claim 33,

wherein said cation is selected from the group consisting of Fe^{2+} , Fe^{3+} , Mn^{2+} , Mn^{3+} , Mn^{4+} , Ca^{2+} , Cu^{2+} , Ti^{3+} , Ca^{++} , and Al^{3+} .

35. The process as claimed in claim 20,

wherein a complexing agent is additionally added to the reaction solution.

36. The process as claimed in claim 35,

wherein said complexing agent is selected from the group consisting of ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentamethylene-phosphonic acid (DTMPA), nitrilotriacetic acid (NTA), polyphosphoric acid (PPA), another iron-, manganese- or copper-complexing agent, diethylamine, and hydroxylamine.

37. The process as claimed in claim 20,

wherein NaOCl is employed.

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38. The process as claimed in claim 20,

wherein a detergent is additionally employed.

39. The process as claimed in claim 38,

wherein said detergent is selected from the group consisting of a nonionic, ionic, anionic, cationic or amphoteric surfactant.

40. The process as claimed in claim 20,

wherein a polysaccharide and/or protein is additionally added to the reaction solution.

41. The process as claimed in claim 40,

wherein a glucan, mannan, dextran, levan, pectin, alginate or plant gum and/or intrinsic polysaccharide formed by the fungi or a polysaccharide produced in the mixed culture with yeasts is employed as the polysaccharide.

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42. The process as claimed in claim 40,

wherein a gelatin and/or albumin is employed as the protein.

43. The process as claimed in claim 20,

wherein a simple sugar, oligomeric sugar, amino acid, polyethylene glycol, polyethylene oxide, polyethyleneimine or polydimethylsiloxane is employed as an additive.

44. The process as claimed in claim 20,

wherein an agent which forms free radicals or an agent which traps free radicals is added to the system.

45. The process as claimed in claim 20,

which is employed for delignification or bleaching of pulp after all the known cooking processes.

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46. The process as claimed in claim 45,

wherein the sulfite, sulfite, organosolv, ASAM process or Enabatch process or other cooking process is carried out as the cooking process.

47. The process as claimed in claim 45,

which is carried out after, between or before all customary bleaching stages and other sequences, such as the Q stage, acid washing and the like.

48. The process as claimed in claim 45,

wherein the process is carried out in several stages, a washing or a washing and an extraction with alkali or neither washing nor extraction taking place between each stage.

49. A multi-component system as claimed in claim 1, for liquefaction of coal.